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A CHEMICAL INVESTIGATION OF AMERICAN SPEARMINT OIL.

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An authentic sample of American spearmint oil distilled from the native herb, *Mentha viridis*, was obtained at the still in Michigan by an inspector of the United States Department of Agriculture. Especial care was taken that the herb used was pure and free from weeds. The object of the investigation was twofold, first, to determine the chemical and physical constants on a pure sample of the oil, and second, to determine the nature of the constituent which carries the characteristic spearmint odor. Elze,¹ working presumably on the German oil, has found the characteristic spearmint odor to be due to dihydrocuminyll acetate, and it seemed desirable, if possible, to verify this on a sample of oil distilled from the American herb.

ANALYSIS OF THE OIL.

An analysis of the oil under investigation afforded the following results:

Specific gravity, 25°/25°=0.9290.

Optical rotation, at 25° C.=−52.16°.

Index of refraction, at 25° C.=1.4866.

Soluble in an equal volume of 80 per cent alcohol.

Carvone by absorption in boiling sodium hydrogen sulphite=66.5 per cent.

by absorption in neutral sodium sulphite=65 per cent.

by titration with hydroxyl amin=66.45 per cent, 66.02 per cent.

Ester number=12.4.

Ester number after acetylation=36.4.

¹ Chem. Ztg., 1910, 37: 1175.

Assuming that the alcohol present has the formula $C_{10}H_{18}O$, these figures correspond to 4.34 per cent ester and to 6.87 per cent free alcohol. This oil differs from many samples which have been examined in this laboratory in respect to the high carvone content. Most of the samples examined have shown a carvone content of about 55 per cent. The carvone recovered from the sulphite liquor had the following constants:

Boiling point (760 mm) = 230.5° or 231° (corrected reading).
 Specific gravity, $25^{\circ}/25^{\circ}$ = 0.9587.
 Optical rotation, at 25° C. = -58.2° .
 Index of refraction, 25° C. = 1.4952.

CONSTITUENTS OTHER THAN CARVONE.

For an examination of the constituents other than carvone, the latter was separated from 2 liters of the oil by means of neutral sodium sulphite and the residual oil was carefully saponified and fractionated at 10 millimeters. The oil was separated into the following fractions:

Under 70° = 385 cc = 19.25 per cent of the oil.
 80– 90° = 8 cc.
 90– 95° = 11 cc.
 95– 100° = 8 cc.
 100– 115° = 155 cc = 7.75 per cent of the oil.
 Residue = 38 cc.

EXAMINATION OF TERPENES.

The fraction distilling under 70° C. contains the hydrocarbons. From it a small fraction was obtained, having an odor suggesting phellandrene and which gave a small amount of phellandrene nitrosite. The terpene left after distilling off the phellandrene was freed from traces of oxygenated constituents by distilling over sodium. It then boiled at 174° to 176° C., optical rotation -54.1° . Limonene is present in this fraction (carvoxim of melting point 71° to 72° C. through the nitroso chlorid). The low optical rotation would indicate that laevo-limonene was not the only hydrocarbon present, however.

THE ALCOHOL FRACTION.

The fraction of boiling point 100– 115° C. at 10 mm had an odor slightly suggestive of linalool, and it was found to consist largely of alcoholic constituents.

For its purification the use of phthalic anhydrid, as recommended by Elze, was found to give a very poor yield of the acid ester. Much better results were obtained by heating to 125° C. with an excess

of succinic anhydrid. By this means 30 grams of the acid succinic ester were obtained from 50 grams of the crude alcohol fraction. The alcohol obtained by saponifying this ester had the following characteristics:

Odor of linalool with a faint suggestion of geraniol.

Specific gravity 20°/20°=	0.9300
N _D (20°C)	= 1.4830
α _D (20°C)	= -22.7°
Boiling point	= 220-221° C.

Oxidized with the dichromate sulphuric acid mixture an oil possessing the odor of dihydrocarvone was obtained. This was purified through its sodium bisulphite addition product. The semicarbazone was prepared—melting point 200° to 201° (when quickly heated); oxim, melting point 88° to 89°. On mixing with the oxim of dihydrocarvone no depression of the melting point was observed. The alcohol is, therefore, dihydrocarveol. Schimmel and Company¹ isolated this alcohol, for the first time from an essential oil, from oil of caraway. They found a boiling point of 100° to 102° (7 to 8 mm), a specific gravity at 15° C. of 0.9368; α_D-6° 14'; N_D at 20° C.=1.48364. Careful search was made for evidence of the presence of dihydrocumyl alcohol in this sample of spearmint oil with negative results.

ACIDS.

The acids were recovered from the saponification liquors. Among the volatile acids present acetic acid predominates (fractional crystallization and analysis of silver salts). There is also evidence of traces of butyric and caproic or caprylic acid as indicated by the odor, while a partial reduction of the silver salts, on boiling, indicates the presence of a little formic acid.

A small amount of acid not volatile with steam was obtained which was separated into a fatty acid and an acid moderately soluble in boiling water from which it crystallizes, on cooling, in small needles. These acids are present in very small and about equal amounts, certainly less than 0.1 per cent of the oil. The crystalline acid has been separated by the writer from three different samples of American oil of spearmint, and appears, therefore, to be a constant ingredient. Recrystallized from alcohol in needles of a pearly luster, it melts at from 182° to 184° C., with slight decomposition. This acid has not yet been further examined.

¹ Report for April, 1905.

As dihydrocarveol proved to be the alcohol present in this oil, it seemed probable that the acetate of dihydrocarveol would give the characteristic spearmint odor. A sample of dihydrocarveol was prepared from carvone and acetylated. The product had an odor reminding one of spearmint. No odor of menthol could be detected in the oil or in any of the fractions examined, though it has been noticed in nonauthentic samples examined in this laboratory, no doubt being due to an admixture of some *Mentha piperita* with the true spearmint herb.

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